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16. ABSTRACT

6.4 Organic Contaminants

Review of Potential Problems

Specific Contaminants: Polychlorinated Biphenyls; DDT and its Metabolites; Aldrin plus Dieldrin; Hexachlorobenzene; Lindane; Chlordane, Methoxychlor; Polynuclear Aromatic Hydrocarbons; Chlorobenzene Compounds; Phenols; Phthalate Esters; Chloronorbornene, Octachlorostyrene; Methylbenzothiopene; Biphenyl; Endosulfan; Cyanide; Heptachlor Epoxide; Other Organic Constituents.

Discussion: Persistent Organic Contaminants; Taste and Odour Compounds

Conclusions.

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JOURNAL ARTICLE

6.4 ORGANIC CONTAMINANTS

REVIEW OF POTENTIAL PROBLEMS

Organic pollutants may constitute the most widespread waste loadings into the waters of Lake Huron. There are essentially three categories of organic contaminants. The first grouping consists of those organic compounds that readily degrade biologically or chemically. Visual perturbations are generally detected after degradation because of sludge deposition and reduced oxygen levels with subsequent suffocation of some forms of aquatic life (1,2). These reactions can also result in the direct mobilization of metals by complexation (3), conversion of inorganic forms of metals to methyl and dimethyl complexes (4-6), and pH and E_h changes in sediment which may mobilize metals, especially manganese (7) and iron (12).

The second category of organic contaminants is comprised of less readily degraded organic compounds which may be directly toxic to aquatic life and to consumers of aquatic life, which may be bioconcentrated to toxic levels, or which may be metabolized to a more toxic form and stored in higher organisms. An excellent example of such compounds is PCB's which not only directly bioconcentrate to toxic levels but are also metabolized to the more toxic hydroxy PCB's (13).

The third category consists of the many organic compounds that can cause taste and odour problems in domestic water supplies or taint the flesh of food fishes. The best known are phenols (1). Phenols can also combine with chlorine during disinfection and bleaching processes to produce chloro-compounds (8) with markedly different properties: generally more toxic and susceptible to bioaccumulation, more persistent in the aquatic ecosystem (9), and with strong odours or taste (9).

Identification of individual organic compounds is difficult in environmental samples, and currently the state of the art is developing. In addition, comparison of data obtained from air, water, sediments, and biota is often difficult.

The analytical methodology employed for all studies was based on extraction of non-ionic compounds. However, the largest group of potential organic contaminants are ionic, as are many metabolites; these were procedurally excluded from analysis. An example of this class of compounds is pentachlorophenol which is widely used for preserving wood, especially in aquatic environments.

Inputs to Lake Huron via atmospheric precipitation (rainfall and snow) and dustfall were not measured for persistent organic contaminants. However, a wide range of persistent organic contaminants, including PCB's, the α and γ isomers of lindane, DDT and its metabolites, hexachlorobenzene, methoxychlor, chlordane, endosulfan, and dieldrin has been detected in atmospheric precipitation in other areas of the Great Lakes Basin (10, 38, 39).

Highly stable organic compounds are spread throughout the ecosystem. Little is known about the chemical and biological cycling and fate of these compounds. This is particularly important because of the specific characteristics of Lake Huron, including its long retention time, the fact that it receives inputs from Lakes Superior and Michigan, and the fact that the water from this lake flows into the Lower Lakes.

The discussion below for specific contaminants is based on material presented in Chapter 4 (nearshore characteristics) and in Chapter 5.6 (open water fisheries), in addition to the references cited. These data unequivocally demonstrate the widespread occurrence of a large number of persistent organic contaminants and the magnitude of the problem associated with these compounds.

SPECIFIC CONTAMINANTS

POLYCHLORINATED BIPHENYLS

PCB's have been recognized as widespread and highly persistent organic contaminants for some years. Their resistance to degradation and lipophilic nature leads to their bioaccumulation and, accordingly, they have been observed in many forms of biota, including man. PCB's from the atmosphere are found adsorbed onto particulate matter, in snow, and in rain (38,39). PCB's present in water accumulate in suspended matter and biota and are either precipitated with sediments or will enter the food chain. Direct toxic effects to aquatic animals, mink, birds, monkeys, and man have been noted (11). Because of their widespread occurrence, persistence, bioaccumulation, and toxicological significance, U.S. and Canadian agencies have developed objectives and guidelines for maximum PCB levels in water, food, and biota for the protection of ecosystems and of man himself. The current guideline levels are given in Appendix C. In addition, the Water Quality Objectives Subcommittee of the Water Quality Board has reported (27) that PCB's in water should not exceed 1 ng/ℓ but this level may not be adequate to provide protection to certain predators and can not be enforced because of insufficiently sensitive quantification limits.

WATER AND SESTON

PCB's were not detected in the waters of Lake Huron at the detection limit ($\sim$10 ng/ℓ) except in Saginaw Bay. Concentrations at the Saginaw River mouth were $\sim$90 ng/ℓ, decreased to $\sim$20 ng/ℓ in the inner bay, and to $<$10 ng/ℓ in the outer bay (Table 4.2-5). Seston was found to contain between 4.9 and 8.1 mg/kg of PCB's at three locations in southern Lake Huron (25); similar residues were observed in Georgian Bay near Collingwood and off the mouth of the Moon River. All other seston samples showed PCB contamination in the order of 1 mg/kg.

FISH

PCB contamination is observed lakewide in Lake Huron fishes. All species examined had PCB residues with the highest level observed in large size predators, including rainbow trout, walleye, and northern pike. In addition, PCB concentrations measured in edible portions of perch appear to be higher in the southern part of Lake Huron.

In the open water fish program, whole fish were analyzed. PCB levels were highest in bloater chub from Alpena (2.61 mg/kg) and in burbot from the Straits of Mackinac (2.35 mg/kg). In slimy sculpins, mean location concentrations ranged from 0.52 to 0.81 mg/kg.

A survey on fish from Saginaw Bay indicated approximate PCB residue means of 0.2 mg/kg in yellow perch, 0.6 mg/kg in suckers, and up to 4.3 mg/kg in edible portions of carp more than 2.5 kg in weight (15). Large brown trout had PCB residues of 1.9 mg/kg; samples of the same species with weights <2.5 kg, taken from the northern part of Lake Huron, had PCB residues of ∿1.1 mg/kg. The edible portion of chinook salmon from Alpena contained an average PCB concentration of 2.31 mg/kg; brown trout from Hammond Bay and from Alpena had average PCB concentrations of 1.13 and 1.10 mg/kg, respectively.

In Ontario nearshore waters, the highest mean location PCB concentrations were found in rainbow trout from Douglas Point (2.18 mg/kg) and Goderich (1.94 mg/kg) (Table 4.1-15) (16). Rainbow trout from Nottawasaga averaged 1.21 mg/kg in edible portions. A direct relationship between weight of rainbow trout and concentration of PCB residues was observed. White suckers from Georgian Bay had PCB residues from 0.3 to 1.2 mg/kg and yellow perch had a mean of 0.2 mg/kg. Both white sucker and yellow perch from the North Channel area showed mean PCB concentrations of approximately 0.1 mg/kg (16).

The mean concentrations of PCB's in several fish species from several locations approach or exceed the Canada health protection guideline of 2.0 mg/kg and the U.S. Food and Drug Administration (FDA) guideline of 5.0 mg/kg for edible portions of fish. In addition, individual rainbow trout from Goderich, Owen Sound, Thornbury, and Nottawasaga Bay contain PCB's which exceed the 2.0 mg/kg Canadian guideline. This is particularly evident in larger, older fish. Practically all fish contain PCB concentrations in excess of the 0.1 mg/kg proposed Agreement objective for PCB's in whole fish. Much of the available data are given as residues in edible portions of fish and, because of the strong association of PCB's with adipose tissues in inedible portions of fish, the actual total body burdens should be considered as even higher.

SEDIMENTS

Detectable amounts of PCB's were found in sediments from the Ausable River (Ontario) mouth and at Bayfield (36 to 94 µg/kg). Levels in Georgian Bay sediments ranged from less than the detection limit to 900 µg/kg; concentrations >100 µg/kg were found in Owen Sound and in Collingwood Harbour (Table 4.1-7). Some of the sediments in the North Channel contained trace amounts of

PCB's but an average of 68 µg/kg was found in the Spanish River mouth. The only U.S. location with PCB's detectable in the sediments was Harbor Beach (18 to 27 µg/kg).

SOURCES

The contamination of Saginaw Bay with PCB's results from their discharge to the Saginaw River and its tributaries. The Saginaw River has the highest PCB concentration of any river tested in Michigan. The major and several of the minor point sources have been identified and corrective action initiated at the source. Data collected subsequent to these actions show a continuing elevated level in both water and fish, indicating significant input remains from non-point sources.

Although PCB input into the Upper Lakes is definitely associated with industrial and municipal effluents (Chapter 3.2) (18, 19), total loadings from these sources and from tributaries do not account entirely for the PCB residues observed in the sediments and the biota of these waters, nor for their widespread distribution. From limited investigations on PCB's in rain (10,38,39) it is known that PCB's are present in precipitation; the observed concentrations of less than or near 0.02 µg/ℓ (including particulate fallout) may account for an input of 1,000 kg/a to Lake Huron.

Chlorinated biphenyl compounds have affected the fishery of Lake Huron. Continued inputs of PCB's may entirely eliminate the use of fish as a food source. Immediate and decisive steps must be taken to prevent further contamination and degradation.

DDT AND ITS METABOLITES

DDT and its metabolites (DDD and DDE) were the first of the general group of compounds known as chlorinated hydrocarbon insecticides to receive worldwide attention as a highly persistent contaminant present in practically all trophic levels of the environment. DDT's are particularly known for their bioaccumulation characteristics in aquatic organisms, their effects on fish and wildlife, and their potential carcinogenicity in humans. Reported as present in fishes of the Great Lakes during the mid-1960's (20), DDT was banned from use in the states bordering on Lake Michigan during 1969-70, essentially banned in Canada in 1970, and banned in the entire United States in 1972. Since the control on DDT usage by the states bordering on Lake Michigan, average residues of this insecticide have declined dramatically in that lake (21) and in the Lower Lakes in general. Current recommended guidelines or criteria for maximum allowable concentrations of DDT in water and the aquatic biota are given in Appendix C.

WATER

Only limited data are available for DDT in water. Detectable levels in the 0.001 to 0.004 µg/ℓ range have been recorded at DeTour, Cheboygan, Presque Isle, and Lexington.

FISH

The average lake-wide concentration of DDT in large, whole bloater chubs collected as part of the open water program was 2.85 mg/kg with the highest values occurring at Alpena (4.37 mg/kg) and the Straits of Mackinac (3.52 mg/kg) (Table 5.6-6). The highest values in burbot (1.77 mg/kg) were recorded at the Straits of Mackinac (Table 5.6-7). Values for slimy sculpin were relatively uniform across Lake Huron, ranging from 0.60 to 0.76 mg/kg (Table 5.6-5). A limited sampling program in the mid-1960's showed that bloater chub from Lake Huron contained 3.6 mg/kg of DDT (20).

DDT was generally detectable in the edible portions of all fish from nearshore waters (Table 4.1-15). Mean location concentrations in Michigan waters of Lake Huron were all >0.2 mg/kg for the salmonids; the highest location mean was 0.97 mg/kg in chinook salmon from Alpena. The maximum location mean in Ontario nearshore waters was 0.723 mg/kg for white suckers from Nottawasaga Bay.

The Canada and the U.S. health protection guideline for DDT in the edible portions of fish is 5 mg/kg; the proposed Agreement objective is 1.0 mg/kg for whole fish. Thus, virtually all of the fish from Lake Huron are within the current health protection guidelines but many species of fish, especially whole fish from the open waters, exceed the proposed Agreement objective. Although only fillets of other fish such as trout and salmon were analyzed, it appears probable that some of these species may also exceed the proposed Agreement objective if whole fish were analyzed.

Comparison of average DDT levels in bloater chubs, sculpins, rainbow trout, whitefish, walleye, yellow perch, and northern pike taken from Lake Superior and Lake Huron suggest that DDT levels are as high or higher in Lake Huron than in Lake Superior.

SEDIMENT

Small amounts of DDT and/or its metabolites were detected in the sediments from several locations in Lake Huron, including Tobermory, Owen Sound, Collingwood, Penetang, Midland, the Spanish River mouth, Serpent Harbour, Harrisville (3.0 µg/kg), Presque Isle (16.3 µg/kg), Alpena (3.9 to 30.7 µg/kg), and Cheboygan (7.2 µg/kg).

SOURCES

DDT levels can generally be attributed to past agricultural uses. Levels present at the Spanish River mouth and in Serpent Harbour are derived from past usage for control of black flies. If continued sources of this compound are causing the residue levels to remain high, then monitoring, including atmospheric sampling, should be continued to locate and possibly eliminate the contamination. Possibly the chemistry of the water mass itself is responsible for the detection of isomers of DDT, particularly DDE, in the system.

ALDRIN PLUS DIELDRIN

Aldrin is metabolically converted to dieldrin by aquatic organisms and by direct oxidation. Dieldrin is considered to be as toxic or slightly more toxic than aldrin to aquatic organisms. Further, it is highly persistent, bioconcentratable, and a potential human carcinogen. Because of these characteristics, the U.S. Environmental Protection Agency (EPA) suspended the production and use of both aldrin and dieldrin in 1974. Dieldrin was first reported as present in fishes of the Great Lakes in the late 1960's (20) and routine evaluation of dieldrin levels in Lake Michigan fish since 1969 by the U.S. Fish and Wildlife Service has shown no significant change in average residue levels (21). Guidelines or criteria for maximum allowable concentrations of aldrin and/or dieldrin in water and the aquatic biota are given in Appendix C.

WATER

Dieldrin has been detected in Saginaw Bay, with concentrations ranging from 0.8 ng/ℓ at the mouth of the Saginaw River to 0.6 ng/ℓ in the outer bay. The proposed Agreement objective for aldrin plus dieldrin is 1 ng/ℓ for the protection of fish and aquatic life. The Michigan State standard for raw water is 17 µg/ℓ.

FISH

Reinert (20) reported dieldrin residues in whole fish ranging from 0.02 to 0.12 mg/kg in a number of fish species collected from Lake Huron in 1967-68. Whole fish samples from the present study (Chapter 5.6) contained mean location concentrations of dieldrin between 0.07 and 0.38 mg/kg. Residues were generally higher in fish from the Straits of Mackinac, Alpena, and Goderich.

Mean dieldrin concentrations in edible portions of fish from Michigan nearshore waters of Lake Huron ranged from less than the detection limit (0.01 mg/kg) to 0.05 mg/kg; similarly, the range for fish from Ontario nearshore waters was from <0.001 to 0.045 mg/kg. Levels were highest in predator species. Aldrin was not detected in Ontario nearshore fish.

The U.S. FDA guideline for dieldrin is 0.3 mg/kg for the edible portion of fish; the proposed Agreement objective for aldrin plus dieldrin in the edible portion of fish is 0.3 mg/kg. No dieldrin residues were found to exceed this limit for edible portions of fish. Some whole fish have mean location concentrations up to 0.38 mg/kg, which implies that levels in the edible portions are elevated but probably do not exceed the limit.

SEDIMENT

Dieldrin was only detected in sediments in the nearshore (segment D) area of Georgian Bay, in Owen Sound Harbour, and at Penetang-Midland.

SOURCES

A possible source of dieldrin is agricultural use. Dieldrin has been detected in precipitation (39).

Because elevated levels have been found in whole fish from Lake Huron and because of the persistence of this compound at concentrations equal to or greater than levels reported in 1967-68, additional monitoring of tissue burdens is needed. The effects of this compound on the ecosystem have not been assessed and should be studied.

HEXACHLOROBENZENE

Hexachlorobenzene was found in burbot (whole fish) from the Straits of Mackinac and from Goderich in the concentration range of 0.01 to 0.5 µg/g (Table 5.6-9) (22). Analyses in water and effluents were not performed or were reported as less than detection limits depending upon the methodology employed.

No safe levels have been established in water or tissue for this compound; however, no significant bioactivity is known. Uses include the conversion to pentachlorophenol, a universally accepted wood preservative, as a fungicide, and in the manufacture of rubber for tires and other chemicals (24).

The ecological significance of this widespread non-degradable compound should be determined. Concentrations in effluents, water, biota and the atmosphere should be monitored to determine sources and possible effects on aquatic life. Safe levels should be established in food containing this compound, since its presence is now known but the associated hazard is not.

LINDANE

The γ-isomer of lindane is the active component in hexachlorocyclohexane. Low levels (0.01-0.04 mg/kg) have been found in whole fish from Lake Huron but well below the proposed Agreement objective of 0.3 mg/kg for lindane in edible portions of fish. In addition, trace amounts (up to 0.005 µg/ℓ) of lindane were found in every water sample examined (25). The proposed Agreement objective for lindane in water is 0.01 µg/ℓ. Lindane has also been detected in precipitation samples collected in the Great Lakes Basin (39).

Because of the extreme persistence of this compound and its continued use, monitoring concentrations in fish and fish-consuming animals is needed. The ecological effects of lindane are unstudied in Lake Huron and effort should be made to determine the significance of widespread observations of trace levels.

CHLORDANE

Technical grade chlordane is a mixture of different compounds of which the α- and γ-isomers represent ~20% each. These two isomers, both persistent, are reported frequently as "chlordane," either separately or collectively, in environmental samples together with smaller amounts of nonachlor isomers and the metabolite oxychlordane. The use of this preparation is now suspended in the United States although it is permitted for limited agricultural use in Canada.

Movement from soil into aquatic ecosystems by surface runoff or ground water has been demonstrated (28,29); these substances can also enter the aquatic ecosystem in precipitation (39).

Chlordane has been sought for in the waters, seston, and sediments of Lake Huron at quantification limits of 0.01 µg/ℓ, ∿0.1 mg/kg, and 0.005 mg/kg, respectively. None was observed (25). Chlordane has been found in the edible portions of fish from the Ontario nearshore waters of Lake Huron with values highest in predator fish from southern Lake Huron (14.0 µg/kg) and Georgian Bay (9.1 µg/kg) and lowest for the North Channel-Lake George area (0.8 µg/kg). This pattern of lowest values in the North Channel-Lake George area also holds for yellow perch and suckers.

Whole fish were collected as part of the open water program. Sculpin from the Straits of Mackinac and burbot from the Straits of Mackinac and Goderich contain an average of 0.14 to 0.18 µg/g of chlordane. Bloater chubs from the Straits of Mackinac and from Goderich have average concentrations of 0.30 and 0.49 µg/g, respectively. Nonachlor isomers were also noted in both burbot and bloater chub and oxychlordane in burbot from the Straits of Mackinac.

Since no objective to protect consumers of fish and aquatic life has been proposed, it cannot be concluded whether a problem exists or not. The observed levels are of concern and sources, particularly in the southern part of the lake, must be identified. Work is required to delineate the extent of aerial deposition.

METHOXYCHLOR

Methoxychlor is used for the control of agricultural pests and of biting insects. This compound may be lost to the environment by volatilization and has been detected in precipitation (39); it does not readily leach from soils (30). The proposed Agreement objective is 0.040 µg/ℓ for the protection of aquatic life. This level has not been reached in Lake Huron possibly as a result of degradation to less persistent metabolites and loss to the sediments. Methoxychlor has been looked for (25) but not found in any of the water, seston, or sediment samples (quantification limits 0.01 µg/ℓ, ∿1 mg/kg, and 0.01 mg/kg, respectively) in Lake Huron. Examination of fish samples (fillet portions) of the Upper Lakes has been made for methoxychlor (33), but it was not detected at levels above 2 µg/kg. It is, therefore, not considered to be a problem in this area. In offshore fish of both lakes, <50 µg/kg was found in all samples (whole fish).

Continued monitoring in water, fish, and the atmosphere is needed as usage of this material increases, especially in high application areas.

POLYNUCLEAR AROMATIC HYDROCARBONS

The polynuclear aromatic hydrocarbons naphthalene, methylnaphthalene, phenanthrene, and methylphenanthrene have been found in the approximate range of 0.01 to 0.5 µg/g, total, in whole fish samples from both U.S. and Canadian sampling stations (Table 5.6-9) (22). Polynuclear aromatic hydrocarbons are often present in industrial effluents containing oil and grease. Large loadings

of both oil and grease to water have been computed as a result of man's activities (18,19), and these compounds have been identified in effluents from petroleum refining, coal processing, and coke manufacture (24). These compounds may be accompanied by other, even less desirable polynuclear aromatic hydrocarbons.

No safe levels for these compounds have been determined in fish tissue but maximum levels for the protection of aquatic life are 0.01 mg/ℓ total hydrocarbons and for domestic water supply to be "virtually free" from oil and grease. In addition, polynuclear aromatic hydrocarbons have been demonstrated as carcinogenic in test animals at relatively high exposure levels.

This class of compounds should be measured in effluents and aquatic biota to determine sources, and possible effects on fish-consuming animals, including man, should be investigated. Since their presence has now been discovered in food, safe levels should be established for human consumption.

CHLOROBENZENE COMPOUNDS

Tri-, tetra-, and pentachlorobenzene were found in burbot (whole fish) from Goderich (Table 5.6-9) (22) in total concentrations of ∿0.01 to 0.5 µg/g. Trichlorobenzene was also detected in burbot from the Straits of Mackinac. No safe levels have been established in water or food for chlorobenzenes. Their uses include solvents for high-melting chemicals such as dyes and insecticides (termite preparations) and as lubricants and heat transfer media (24).

These compounds are very persistent and in view of their widespread use and resulting fish contamination, they should be monitored to determine sources and possible effects on aquatic life and consumers of aquatic life, including man. Since they have been detected in food, safe levels should be established for human consumption.

PHENOLS

Phenol and other compounds that can cause taste and odour problems have been measured in many effluents discharging to the lake and have been found at levels exceeding the proposed Agreement objective (1 µg/ℓ) and the Ontario criterion for water supply at Parry Sound Harbour (2 out of 13 samples were 2 and 5 µg/ℓ), the Spanish River mouth, and the St. Marys River. At the Spanish River mouth, the average and maximum concentrations during a June 1974 survey were 3 and 14 µg/ℓ, respectively; corresponding values during a May 1975 survey were 1.3 and 2 µg/ℓ. The source is the Eddy Forest Products mill at Espanola; in 1973 the average phenol discharge was 140 kg/d. This may be contributing to reports of fish tainting in the area.

The phenol discharge from Algoma Steel at Sault Ste. Marie averaged 200 kg/d in 1974. The average concentration 0.3 km downstream from the outfall was 24 µg/ℓ; this decreased to ∿10 µg/ℓ at 3.2 km downstream and persisted at least 11 km downstream into the Lake George Channel where transboundary movement of phenols is evident. The concentration in the St. Marys River is augmented by the 23 kg/d discharge of phenols from Domtar Chemical via the Sault Ste. Marie, Ontario, sewage treatment plant.

Phenols are biodegradable; however, if they are present in water during disinfection or bleaching processes, they may form polychlorinated compounds (8). These compounds are much less degradable, are toxic to bacteria and other aquatic life, have greater potential for bioaccumulation (9), and are more objectionable in taste and odour production. The polychlorinated compounds may form chloroanisoles due to methylating action of some bacteria; these compounds are detectable in water and fish flesh at very low levels (36).

Proper treatment of wastes containing these compounds before chlorination will eliminate both taste and odour problems in domestic water supplies and fish tainting problems. Bleaching processes using chlorine pose a special problem. Monitoring of effluents for the polychlorinated phenols and related compounds should be done routinely. In view of the magnitude of the wastes which contain phenols, analysis of these compounds and their chlorinated derivatives in fish flesh should be undertaken to determine the extent to which the biota may be contaminated.

PHTHALATE ESTERS

Phthalate esters are extensively employed as plasticizers in plastics manufacturing and processing. Recently, phthalates have been detected in many industrial and municipal discharges in the Great Lakes area ranging as high as 1.2 µg/ℓ (26). Phthalates have been detected in settleable solids at levels as high as 75 µg/g (dry weight). It is likely that these values represent a minimum level (excluding contamination) since phthalate esters can occur as conjugates (17) which are not likely to be extracted by normal analytical techniques. These esters may be readily eliminated on exposure to clean waters (17). Chronic toxicity considerations (1) resulted in proposed Agreement objectives of 4.0 µg/ℓ for dibutyl phthalate, 0.6 µg/ℓ for di(2-ethylhexyl)-phthalate, and 0.2 µg/ℓ for other phthalate esters for the protection of aquatic life; these levels are only slightly above the analytical capabilities of monitoring laboratories.

Phthalates are noted (1) in nearshore and offshore waters of the Upper Lakes. Four samples from Saginaw Bay had concentrations of di(2-ethylhexyl)-phthalate ranging from <1 to 1.4 µg/ℓ with a mean of 1.3 µg/ℓ, in excess of the proposed Agreement objective. The sources are upstream discharges to the Saginaw River and its tributaries. Several phthalates were sought but not found in fish from nearshore waters of Michigan. Diethyl-, dibutyl-, and di(2-ethylhexyl)phthalate have been detected in whole fish samples of burbot from both the Straits of Mackinac and Goderich in the concentration range of 0.01 to 0.1 µg/g (Table 5.6-9).

Since phthalates cannot as yet be associated with deleterious effects, they are not considered to be a major problem. They should, however, be monitored in waters receiving municipal and industrial discharges until such time as feeding experiments can establish no-effect levels.

CHLORONORBORNENE

Chloronorbornene and related compounds similar to those in toxaphene were identified in whole-fish samples from both U.S. and Canadian open-lake sampling stations at concentration levels in the approximate range 0.1 to 1.0 µg/g (22). The presence of similar compounds has been established in water adjacent to and downstream of a kraft pulp mill effluent (35).

No safe levels have been determined in food or for fish-consuming animals. Because of the observed levels in open lake fish and the fact that direct sources of these compounds are at this time undetermined, monitoring of these compounds in effluents and aquatic life is recommended.

OCTACHLOROSTYRENE

Octachlorostyrene was found in fish from Saginaw Bay and in burbot (whole fish) from Goderich (22,34); the concentration at the latter location was in the 0.001 to 0.01 µg/g range (Table 5.6-9). No safe level has been established for the compound. The only previous reports of the contaminant come from Europe (32). Sources of this compound are not generally known but it is a suspected by-product in the manufacture of perchlorinated solvents (34).

Because of its apparent inertness and ability to bioaccumulate, this compound should be studied to determine if there are sources to Lake Huron and possible effects on the biota. Consideration should be given to establishing criteria for food products.

METHYLBENZOTHIOPHENE

Methylbenzothiophene has been found in burbot (whole fish) from the open waters off Goderich in the approximate concentration range of 0.01-0.1 µg/g (Table 5.6-9) (22). No safe levels have been established for the compound in fish or water. Benzothiophene is a contaminant in coal products and will leach from coal processing residue (24). Sources and bioactivity of this compound should be investigated.

BIPHENYL

Biphenyl was found in burbot (whole fish) from the open waters off Goderich (22) (Table 5.6-9) in the concentration range of 0.01 to 0.1 µg/g. Biphenyl is known to be often present in industrial effluents containing oil and grease. Large loadings of both oil and grease to water have been computed as a result of man's activities (18,19), and this compound has been identified in effluents from petroleum refining, coal processing, and coke manufacture (24). Biphenyl mixtures may be expected to be accompanied by other, even less desirable polynuclear aromatic hydrocarbons.

No safe levels of these compounds have been determined in fish tissue but criteria for the protection of aquatic life are 0.01 mg/ℓ total hydrocarbons. Criteria for domestic water supply indicate that the water supply should be "virtually free" from oil and grease.

Biphenyl is used as a dye carrier in the textile industry and may be present from oil refining or coal processing. Possible occurrence in chlorinated water supplies or municipal wastes could result in the formation of chlorobiphenyl as a result of disinfection (8).

Biphenyl should be measured in effluents and aquatic biota to determine sources, and possible effects on fish-consuming animals, including man, should be investigated.

HEXABROMOBIPHENYL

Hexabromobiphenyl, one of the family of compounds known as PBB's, is used as a flame retardant. Hexabromobiphenyl was produced by the Michigan Chemical Company at St. Louis, Michigan. It has been found contaminating meat and milk in Michigan but has not yet been detected in the nearshore fisheries of western Lake Huron. Hexabromobiphenyl has been found, however, in fish tissues at levels exceeding the U.S. FDA guideline of 0.3 µg/g for 40 km downstream from the plant discharge into the Pine River (14). Migratory fish from this river could be contaminated and contaminated sediment may move downstream and affect lake fisheries.

Monitoring for this compound and others which are used as flame retardants should be continued to determine possible future problems.

ENDOSULFAN

Endosulfan is employed extensively as an agricultural pesticide and it may be present in agricultural runoff for short periods (1-2 weeks) after application (31). In addition to runoff, aerial deposition can introduce this compound into the surface waters of the Great Lakes (10,39) presumably both to nearshore areas and the open lake. However, under the aerobic, slightly alkaline conditions normally observed in Lake Huron, it is not expected to persist but rather to degrade at least to either the endosulfan sulphate (23) or diol (31). These compounds have not been reported in organisms of Lake Huron. Consequently, no identifiable problem is associated with the use of endosulfan. It should be noted that the examinations for these three compounds have not been extensive and receiving waters of agricultural drainage should be examined more thoroughly.

These compounds have not been observed in any water, seston, or sediment samples in Lake Huron (25) above levels of 0.01 µg/ℓ, ∿0.2 µg/g, and 0.01 µg/g, respectively. However, because of the high toxicity, monitoring is suggested in areas where this compound is used and studies should be initiated to determine breakdown products and metabolites in the Great Lakes.

CYANIDE

Cyanide loadings attributable to Algoma Steel at Sault Ste. Marie amounted to 2280 kg/d during 1974; the total input to Lake Huron is ∿2800 kg/d. The cyanide concentration averaged 0.28 mg/ℓ near the Canadian shore just downstream from the main trunk sewer and levels diminished to 0.06 mg/ℓ at 1 km

downstream and to 0.03 mg/ℓ in the Lake George Channel (Figure 4.3-6). These levels exceed the proposed Agreement objective of 0.005 mg/ℓ; the Ontario permissible criterion for raw water, 0.2 mg/ℓ, (Appendix C) is violated for 0.3 km downstream from the outfall. In general, levels during 1973-74 were higher than in previous years mainly due to low flow conditions in the St. Marys River. Little or no data are available to determine the possible effects of the cyanide loading on the lake ecosystem and studies are needed to determine if other than localized effects have occurred. Possible synergistic effects of cyanide on the biota in the St. Marys River with other contaminants, including heavy metals, phenol, and ammonia, should be investigated.

HEPTACHLOR EPOXIDE

The proposed Agreement objective for heptachlor plus heptachlor epoxide in the edible portions of fish is 0.3 µg/g for the protection of human consumers of fish (1,2); see Appendix C. Heptachlor epoxide was found in burbot (whole fish) from the Straits of Mackinac in the approximate concentration range of 0.1-1.0 µg/g. Although analysis of edible portions of fish indicate concentrations lower than present guideline levels, continued monitoring of this persistent chemical is needed to determine sources and residue levels satisfactory for human consumption.

DISCUSSION

All organic contaminants have the potential to adversely affect aquatic resources by either reducing the survival, growth, and reproduction of fish and fish food organisms or rendering the water and/or fisheries of Lake Huron unfit or unsafe for consumption by higher life forms.

PERSISTENT ORGANIC CONTAMINANTS

The dispersion of persistent organic contaminants throughout the Lake ecosystem occurs both within the lake and through atmospheric transport. Whole-lake degradation is clearly indicated. Atmospheric inputs appear to be a significant source since several of the compounds were found at comparable levels in both Lake Superior and Lake Huron. Further evidence of atmospheric transport is indicated by the presence of similar concentrations of such persistent organic compounds as PCB's, hexachlorobenzene, heptachlor epoxide, and methoxychlor in fish from Lake Superior and in fish from Siskiwit Lake, an inland lake on Isle Royale which has received no known direct discharges of these compounds (37,40).

A wide range of organic constituents found in whole-fish samples of burbot from the Straits of Mackinac and Goderich is given in Table 5.6-9. Several of these are new in reports of Great Lakes contaminants. Of greatest concern is the fact that many of these compounds are noted for their stable characteristics and long lives in aquatic systems. They can only be attributed to products of man and his activities. Too little is known regarding chronic effects to permit any estimate of the direct risk to fish stock or to wildlife and man as a consumer of this low level contamination. Still less is known of the pathways by which they reach fish and the effects which they may have on other components of the aquatic ecosystem and hence indirectly on fish.

Regardless of the absolute concentrations of this wide array of chlorinated hydrocarbons found in water and biota of the Upper Lakes, the Reference Group is concerned over the common presence of numerous toxic organics whose individual effects, acute or chronic, toxic or sublethal, are poorly known and whose potential combined effects are completely unknown both in the aquatic biota and in organisms which depend on them for food. It is apparent that Lake Huron is being contaminated with persistent toxic organic compounds from essentially unknown sources. Past efforts to control DDT contamination, although effective in Lake Michigan, appear to not have had as much effect as yet in Lake Huron. Further contamination of the biota by PCB's and, to a lesser degree, dieldrin is still considered unavoidable in the Upper Lakes. There is also a real potential that if pollution by toxic organics continues unchecked, the fisheries may eventually be lost because of public health problems or, in the extreme, actual loss of the resource from the lakes. This evidence indicates apparent ineffectiveness of controlling toxic organics through partial bans. The only answer is total bans.

TASTE AND ODOUR COMPOUNDS

Excessive levels of taste and odour causing compounds are traceable to industrial discharges into the Spanish River and the St. Marys River. Remedial programs are required at Algoma Steel and Domtar Chemical at Sault Ste. Marie and at Eddy Forest Products at Espanola in order to reduce present discharges of taste and odour causing compounds to levels in compliance with the proposed Agreement objective and the Ontario criteria. The technology is presently available to achieve this abatement.

CONCLUSIONS

The Reference Group concludes that a total ban should be implemented on the manufacture, sale, transport, and use of PCB's, aldrin, dieldrin, and DDT and its derivatives. For other man-made organics such as halogenated hydrocarbons, an accelerated program is required to evaluate effects on human health and biota, to establish a better basis for criteria, and to develop remedial programs as needed. Until the effects are fully understood, there should be no increased manufacture, use, or discharge of these compounds. Further, before new organic compounds are produced, distributed, or used, environmental and health effects should be fully evaluated. Because persistent organic contaminants have been detected in precipitation, monitoring of atmospheric inputs should be routinely conducted. Programs to minimize pesticide use should also be implemented. In addition, remedial measures should be undertaken to eliminate the taste and odour causing compounds.

CHAPTER 6.4

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